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PCT/GB 2005/000401



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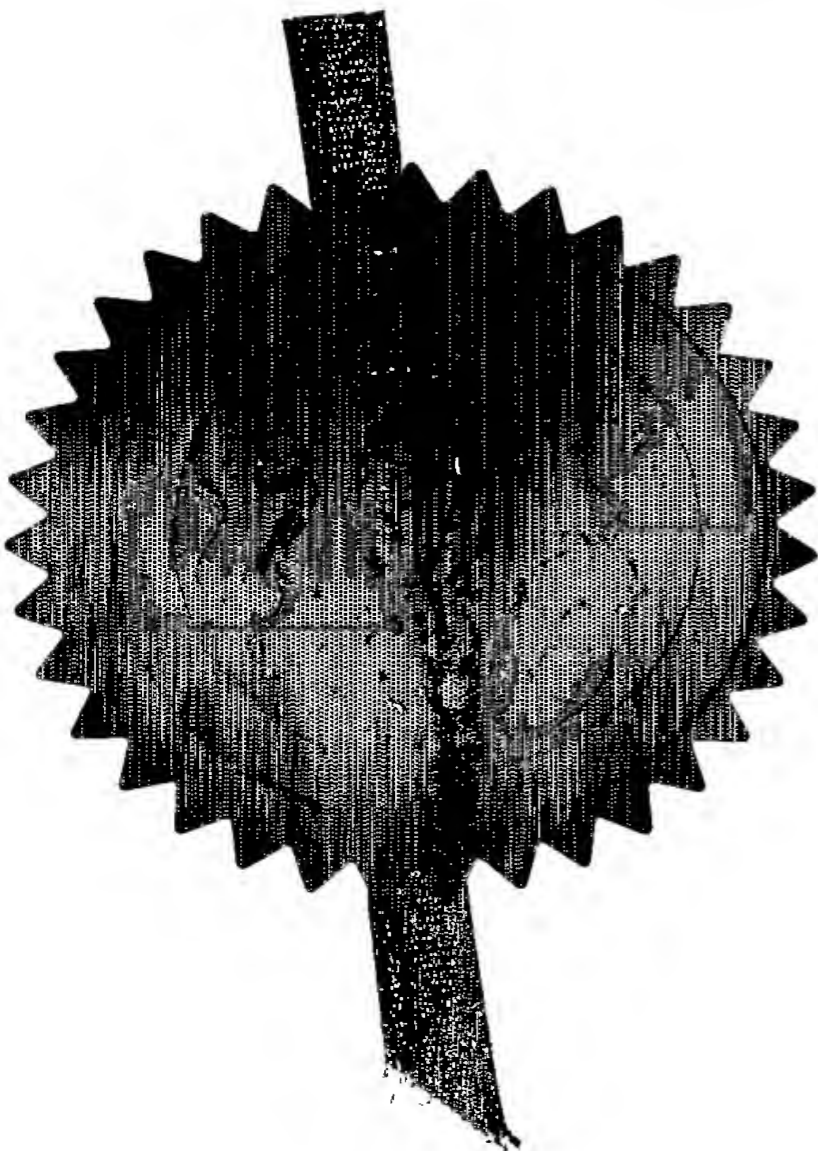
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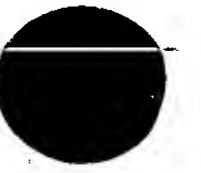


Signed

*Stephen Hordley*

Dated

23 February 2005





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# Request for grant of a patent

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1. Your reference ACH/64889/000

2. Patent application number 0402487.3  
(The Patent Office will fill this part in)

3. Full name, address and postcode of the or of each applicant (underline all surnames) ISIS Innovation Limited  
Ewert House  
Ewert Place  
Oxford  
OX2 7SG

Patents ADP number (if you know it)

8618878002

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention CATALYTIC PROCESS

5. Name of your agent (if you have one) BOULT WADE TENNANT

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

VERULAM GARDENS  
70 GRAY'S INN ROAD  
LONDON  
WC1X 8BT

Patents ADP number (if you know it)

42001

6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)

Number of earlier UK application

Date of filing  
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8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request?

Answer YES if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

Otherwise answer NO (See note d)

Yes

# Patents Form 1/77

- Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description 8

Claim(s) 2

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77) 1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

4 February 2004

12. Name and daytime telephone number of person to contact in the United Kingdom

Adrian C. Hayes  
020-7430-7500

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CATALYTIC PROCESS

The present invention relates to a process involving a  
5 reaction between methanol and hydrogen peroxide to produce a  
gas, in particular a process which uses a catalyst.

Methanol is known to react with hydrogen peroxide. For  
example, JP-A-2001-226102 discloses the simultaneous  
10 reaction of methanol with both water and hydrogen peroxide.  
In order to initiate the reaction in the gas phase over a  
solid catalyst, the reactants are heated to 230°C. The  
reaction is exothermic, so after the reaction has started it  
will continue without additional heat input. However,  
15 hydrogen peroxide may decompose into steam and oxygen at  
such high temperatures before it reacts with the methanol.  
It would be desirable to initiate the reaction without  
heating the reactants to such a high temperature, especially  
to initiate the reaction at a temperature below the boiling  
20 point of the reactants such that the reaction is able to  
occur in the liquid phase. Direct heating is inefficient  
and, in some instances, unavailable, for example when  
reacting the reactants to produce hydrogen in a moving  
vehicle or portable electrical appliance. Furthermore  
25 heating hydrogen peroxide to such a high temperature can be  
dangerous since it is explosive.

We have now discovered a process in which methanol and  
hydrogen peroxide can be directly reacted together without  
30 initially having to heat them to such a high temperature.  
This process utilises a particular catalyst.

Accordingly the present invention provides a process for initiating a reaction between methanol and hydrogen peroxide to produce a gas such as hydrogen, carbon dioxide, carbon monoxide and/or oxygen which comprises contacting methanol and hydrogen peroxide in the liquid phase and at or above atmospheric pressure in the presence of a catalyst comprising at least one group 8, 9, 10 or 11 transition metal.

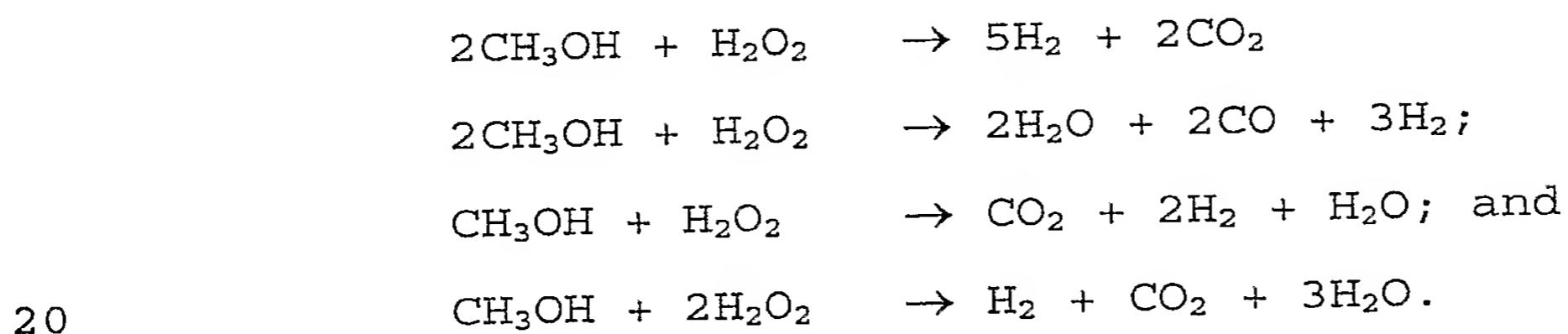
10 In the process of the present invention the reaction between methanol and hydrogen peroxide is initiated by contacting the reactants both in the liquid phase in the presence of a particular catalyst. It has surprisingly been found that little if any heat has to be provided to the system in order  
15 to initiate the reaction. After the reaction is initiated the methanol and hydrogen peroxide continue to react since the reaction is exothermic. Although the catalyst need not remain in the reaction system after the reaction has been initiated, in practice it is usual for the catalyst to  
20 remain in place rather than being removed.

The methanol can be used by itself or in admixture with other components such as, for example, other alcohols or hydrocarbons, for example C<sub>2</sub> to C<sub>4</sub> alcohols such as ethanol,  
25 gasoline, alkanes such as pentane and hexane, diesel or water. Since the reaction is exothermic, once the reaction between methanol and hydrogen peroxide has been initiated, heat is generated which can itself cause a reaction to initiate between additional components such as between  
30 ethanol, gasoline and/or diesel and the hydrogen peroxide or between the methanol and water. For example direct reforming of methanol and water can take place to form

hydrogen and carbon dioxide, optionally together with carbon monoxide.

5 The hydrogen peroxide can be used in pure form, but is preferably used in solution, especially in aqueous solution. It may also be in the form of pellets, such as a urea pellets. Generally the hydrogen peroxide is used in an aqueous solution or pellets comprising at least 10 vol% hydrogen peroxide, preferably at least 15 vol%, more  
10 preferably 20 to 90 vol%, even more preferably 20 to 80 vol%, and most preferably 25 to 60 vol%.

The reaction between methanol and hydrogen peroxide can vary, for example depending upon the stoichiometric amounts  
15 of the reactants which are present. For example the reaction may comprise at least one of, or all of:



The reaction may additionally comprise other reactions such as:



Desirably the methanol and hydrogen peroxide are present in a molar ratio of 2:1 to 1:2, more preferably 1.5:1 to 1:1.5, most preferably about 1:1, especially to increase the yield  
30 of hydrogen.

An additional solvent may be present if desired such as, for example, water. The reactants are contacted in the liquid phase, that is both the methanol and the hydrogen peroxide are in the liquid phase. Of course, during the subsequent  
5 reaction, due to the presence of heat one or more than one of the reactants may be at least partly in the gaseous phase.

The catalyst comprises a group 8, 9, 10 or 11 transition  
10 metal. Thus the catalyst comprises one or more of Fe, Co, Ni, Cu, Tc, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt and Au. The metal is preferably platinum.

The catalyst is preferably promoted, for example with one or  
15 more oxides of alkali metal, alkaline earth metal, rare earth or other transition metals. Examples of suitable promoters are Sn, Ni, Ag, Zn, Au, Pd, Mn and other transition metals in the form of the metal, oxide or a salt. The catalyst may also be modified with one or more further  
20 components, such as boron, phosphorus, silica, selenium or tellurium.

The metal is desirably in elemental form. In order to act effectively as a catalyst it is desirably in particulate  
25 form with a small particle size, as is well known to those skilled in the art. The catalyst may be unsupported. Desirably, however, it is supported, for example on the side of a reaction vessel or tube or on an inert particulate support. For example, very fine nickel or platinum  
30 particles may be plated in an inner layer on a stainless steel tube for methanation in a GC for FID detection.

The support may be any support which is capable of bearing the catalyst in the desired reaction. Such supports are well known in the art. The support may be an inert support, or it may be an active support. Examples of suitable supports are alumina, modified alumina, spinel oxides, silica, modified silica, magnesia, titania, zirconia, a zeolite,  $\beta$ -aluminate and forms of carbon, manganese oxide, lanthanum oxide or a combination thereof. The alumina or modified alumina may be, for example,  $\alpha$ -alumina,  $\beta$ -alumina or  $\gamma$ -alumina.  $\beta$ -alumina and spinel oxides such as barium hexaaluminate have been found to be particularly useful in view of their stability. The carbon may be in the form, for example, of active carbon, graphite or carbon nanotubes. A zeolite may be chosen depending on the desired final product. Thus, for example, it may comprise pores or channels.

Preferably the support is porous. The particle size is desirably 0.2  $\mu\text{m}$  to 0.4 mm. The surface area is desirably greater than 5  $\text{m}^2/\text{g}$ . One or a mixture of two or more supports may be used.

The metal may also be in the form of a complex or compound thereof. Examples are platinum carbonyl complexes and platinum methoxy complexes, and platinum complexes with ligands such as chlorine, phosphine or organic aromatic species such as benzene or cyclopentadiene, such as  $(\text{CO})_5\text{Co}_2(\text{CO})_2\text{Pt}_2(\text{CO})(\text{PPh}_3)_2$  or  $\text{Pt}_3(\text{CO})_2(\text{PPh}_3)_4$ .

Before use, the catalyst may, if desired, be activated, for example with hydrogen or a hydrogen-containing gas.

The initiation can desirably be carried out at about room temperature, for example at about 20°C. Preferably the initiation is carried out without heating the reactants or providing any other source of initiation. However, heat can  
5 be supplied if necessary, although the amount of heat supplied need not be too great. Thus one or both of the reactants, or the reaction mixture, be at, for example, less than 80°C, preferably less than 50°C and more preferably less than 30°C.

10

The reaction between methanol and hydrogen peroxide has a number of uses. For instance when propulsion is needed for a rocket the reaction between methanol and hydrogen peroxide can be used

15

When hydrogen is produced it may be important to restrict the amount of atmospheric oxygen which is available, for example by carrying out the reaction in an enclosed or pressure vessel.

20

When hydrogen is prepared the hydrogen may itself be used in a further process, for example in a fuel cell. Desirably the process of the present invention is carried out in or in association with a fuel cell in order to provide the  
25 hydrogen for a subsequent reaction or can be used to provide a rapid generation of gas and/or heat, for example for use in inflating an air bag, to pressurise mechanical equipment such as a hydraulic or lift, or for the quick start up of a catalytic exhausted gas converter or NO<sub>x</sub> purifier.

30

The present invention is now further described in the following Examples.

**Example 1.**

A mixture of 7ml pure methanol and 21 ml 37%  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  is held in an autoclave, then 40mg of a  $\text{H}_2$ -reduced 5wt%  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  is added to the mixture while stirring. The temperature in autoclave increases from room temperature to 260°C and the pressure in the autoclave increases to 346 psi in 10 seconds. Analysis of the products using an Autosystem GC shows hydrogen, carbon monoxide, methane and carbon dioxide as the products. The hydrogen yield from the reaction is over 85%, and the methanol conversion is 96%.

**Example 2.**

A mixture of 7ml pure methanol and 15 ml 50%  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  is held in an autoclave, then 100mg of a  $\text{H}_2$ -reduced 5wt%  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  is added to the mixture while stirring. The temperature in autoclave increases from room temperature to 290°C and the pressure in the autoclave increases to 360 psi in 10 seconds. The analysis of the products using an Autosystem GC shows hydrogen, carbon monoxide, methane and carbon dioxide as the products.

The hydrogen yield from the reaction is over 90%, and methanol conversion is 98%.

**Example 3.**

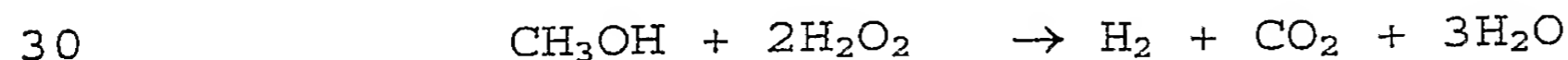
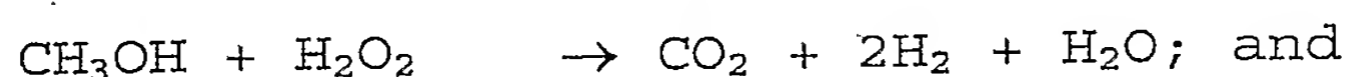
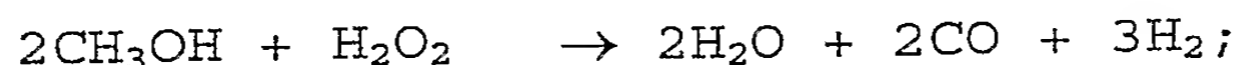
A mixture of 7ml pure methanol and 15 ml 50%  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  is held in an autoclave, then 100mg of a  $\text{H}_2$ -reduced 6wt%  $\text{Pd-Ni}/\text{Al}_2\text{O}_3\text{-MnO}_2$  is added to the mixture while stirring, the autoclave is heated to 50°C while stirring. The temperature

in autoclave increased from room temperature to 220oC and the pressure in the autoclave increased to 330 psi in 15 seconds. The analysis of the products using an Autosystem GC shows hydrogen, carbon monoxide, methane and carbon  
5 dioxide as the products.

The hydrogen yield from the reaction is over 80%, and the methanol conversion is 90%.

CLAIMS

1. A process for initiating a reaction between methanol and hydrogen peroxide to produce a gas, which comprises  
5 contacting methanol and hydrogen peroxide in the liquid phase and at or above atmospheric pressure in the presence of a catalyst comprising at least one group 8, 9, 10 or 11 transition metal.
- 10 2. A process according to claim 1 wherein the hydrogen peroxide is in the form of an aqueous solution or urea pellets comprising at least 15 vol% hydrogen peroxide.
- 15 3. A process according to claim 1 or 2 wherein the reaction between methanol and hydrogen peroxide produces hydrogen.
4. A process according to any one of the preceding claims wherein the methanol and hydrogen peroxide are present in a  
20 molar ratio of 1.5:1 to 1:1.5.
5. A process according to claim 4 wherein the methanol and hydrogen peroxide are present in a molar ratio of about 1:1.
- 25 6. A process according to any one of the preceding claims wherein the reaction comprises at least one of:



7. A process according to any one of the preceding claims wherein the metal is platinum.

8. A process according to any one of the preceding claims  
5 wherein the metal is in elemental form.

9. A process according to any one of the preceding claims wherein the catalyst is supported.

10 10. A process according to any one of the preceding claims wherein the initiation is carried out without heating the reactants.

11. A process according to any one of the preceding claims  
15 wherein the initiation is carried out at a temperature of less than 80°C.

12. A process according to any one of the claims wherein the initiation is carried out at a temperature of less than  
20 30°C.

13. A process according to claim 12 wherein the initiation is carried out at about room temperature.

25 14. A process according to any one of the preceding claims which is carried out in a fuel cell, to power a rocket or to inflate an air bag, to pressurise mechanical equipment or for the quick start up of a catalytic exhausted gas converter or NO<sub>x</sub> purifier.



